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The Wilson equation as a formalism for activity behavior in liquid binary iron-base alloys

William M. Findley
Lehigh University

THE WILSON EQUATION AS A FORMALISM FOR ACTIVITY BEHAVIOR IN LIQUID BINARY IRON - BASE ALLOYS

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WILLIAM M. FINDLEY

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Stephen K. Tarby
STEPHEN K. TARBY
(PROFESSOR IN CHARGE)

Fred P. Stein
FRED P. STEIN
(PROFESSOR IN CHARGE)

C. W. Clump
C. W. CLUMP
(DEPARTMENT HEAD)

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ABSTRACT

The Wilson equation was explored as a possible formalism to explain activity behavior in liquid binary iron-base alloys. A computer program was developed to determine Wilson constants by a best fit of various sets of activity data which appeared in the literature. The process involved selection of the pair of Wilson constants that minimized total deviations between experimental literature activity coefficients and activity coefficients calculated by the Wilson equation. By such a procedure seven systems, which exhibited various types of deviations from Raoult's law, were fit by the Wilson equation. The Wilson equation was found to be capable of correlating all such deviations.

Activity coefficients for five of the seven systems studied were also calculated by Darken's techniques. By calculation of root-mean-square deviations for the systems investigated it was found that Darken's fit was slightly better than that produced by the Wilson equation. However, when the complications and arbitrariness of the Darken approach are considered, it can be concluded that the Wilson equation presents an excellent method of describing activity coefficient behavior in liquid binary iron-base alloys.

INTRODUCTION

Scope

There have been various attempts to formally describe the behavior of activity coefficients for binary systems. Perhaps the most extensive formalism for liquid binary metallic systems has been developed by Darken [1], but his approach is somewhat arbitrary and complicated. Since all efforts to date have had some drawbacks, it is useful to explore the possibility of a new formalism for liquid binary metallic systems.

This research was undertaken to determine whether or not the Wilson equation [2] could be used to describe the activities of the components in liquid binary iron-base alloys. In the past the Wilson equation has been used to describe activities in organic systems.

It was necessary to develop a method of determining the two parameters required to fit a given set of experimental data by the Wilson equation. Once the pair of constants which yielded the best fit for the equation had been calculated, it was possible to directly calculate activity coefficients for the given liquid binary iron-base system being considered.

Activity coefficients calculated by means of the Wilson equation were compared with experimental values for each of the systems investigated. Root-mean-square deviations for activity coefficients fit by the Wilson equation as compared with experimental data are presented. Also, as a comparison of the fit obtained by the Wilson equation with the fit produced by Darken's approach, root-mean-square deviations for data calculated

by Darken s formalism as compared with experimental data are also presented. Then by comparison of the root-mean-square deviations and consideration of calculational procedures, the relative merits of the approach to be presented in this report as compared with Darken's formalism can be determined.

Background

Before discussing the important formalisms of the past, the reasons for interest in activity coefficients of liquid binary iron-base alloys should be mentioned. Activity coefficients are useful thermodynamic quantities because they take into account not only stoichiometric relationships but also mutual attractions between molecules, and interactions between solute and solvent.

With a knowledge of activity coefficients, hence activities, useful thermodynamic quantities such as Gibbs free energies can be calculated. Hence, the importance of activity coefficients as a basic thermodynamic quantity can not be overestimated. It therefore follows that a technique that can calculate values of activity coefficients over a wide range of compositions would be most useful. As far as steelmaking operations are concerned, alloy behavior at low concentrations is of particular interest.

Several significant attempts to predict the behavior of activity coefficients in binary systems have been made. Only a brief mention of the main points of these efforts will be made with the exception of

Darken's formalism. His approach will be discussed in detail in a later section. The earliest effort to represent the activity coefficients of a binary system was by Margules [3] in 1895. He proposed a power series expansion as follows:

$$\ln \gamma_1 = \alpha_1 x_2 + 1/2\ \alpha_2 x_2^2 + 1/2\ \alpha_3 x_2^3 + \cdots$$

$$\ln \gamma_2 = \beta_1 x_1 + 1/2\ \beta_2 x_1^2 + 1/3\ \beta_3 x_1^3 + \cdots$$

to correlate activity coefficient behavior. In 1921 Porter [4] set forth a quadratic approximation to describe certain nonelectrolyte systems. Porter's efforts are expressed by the following:

$$\ln \gamma_1 = \alpha x_2^2 \qquad \text{and} \qquad \ln \gamma_2 = \alpha x_1^2$$

A third approach for representing the thermodynamics of binary solutions was presented by Hildebrand [5] in 1927. In this proposal Hildebrand employs solubility parameters and volume fractions. The solubility parameter is obtained by dividing the molal energy of vaporization by the molal volume. Hildebrand's proposals had success in describing many binary organic systems, but for metallic solutions, which are often exothermic, the solubility parameters are not adequate.

Herzfeld and Heitler [6] had yet a different approach for describing thermodynamic behavior of binary systems. This approach was the quasi-chemical method. In this presentation the solution energy is a linear function of the total types of bonds between nearest neighbor atoms. After several approximations a quadratic expression results, but often because of the assumptions that must be made the results are not good.

The most recent attempt to formalize the behavior of activity coefficients in liquid binary metallic systems has been presented by Darken. His approach involves division of the concentration range into three regions. Then each region is fit by a different expression.

THE WILSON EQUATION

In 1963 Wilson [2] proposed a flexible model, which is suitable for a variety of nonideal mixtures and requires only two parameters to fit a binary mixture. It has been tested by numerous sets of experimental data for both binary and multicomponent systems. The results have been impressive, but until now there has been no attempt to fit binary metallic solution data.

When Wilson extended the theoretical equation of Flory and Huggins, he considered mixtures of molecules that differ not only in size but also vary in intermolecular forces. The Flory-Huggins equation is represented by the following:

$$\frac{g^E}{RT} = \sum_{i=1}^{N} x_i \ln \frac{\phi_i}{x_i} \qquad (1.)$$

where ϕ_i = volume fraction of i

x_i = mole fraction of i

g^E = excess Gibbs energy

R = universal gas constant

T = temperature

and ϕ_i is expressed by the following:

$$\phi_i = \frac{x_i \, v_i^L}{\sum_{i=1}^{N} x_i \, v_i^L} \qquad (2.)$$

where v_i^L = molar liquid volume of pure i

When all components in a solution have the same molar liquid volume, $\phi_i = x_i$. For this case the Flory-Huggins equation predicts ideal behavior.

For a binary solution of components 1 and 2, Wilson expressed the probability of finding a molecule of type 2 compared to finding a type 1 molecule about a central type 1 molecule by the following:

$$\frac{x_{12}}{x_{11}} = \frac{x_2 \exp - [\lambda_{12}/RT]}{x_1 \exp - [\lambda_{11}/RT]} \qquad (3.)$$

The above expression gives the ratio of the number of type 2 molecules about a type 1 molecule to the number of type 1 molecules about a type 1 molecule as the ratio of mole fractions of component 2 to component 1, each weighted statistically. The statistical weighting is accomplished by the two Boltzmann factors. Also the probability of finding a type 1 molecule to finding a type 2 molecule about a central type 2 molecule is given by the following:

$$\frac{x_{21}}{x_{22}} = \frac{x_1 \exp - [\lambda_{12}/RT]}{x_2 \exp - [\lambda_{22}/RT]} \qquad (4.)$$

In light of the above equations Wilson has empirically redefined the volume fraction terms that appear in the Flory-Huggins equation. As Wilson has redefined these terms they are called local volume fractions and are shown by the following equations:

$$\psi_1 = \frac{x_1 v_1^L \exp - [\lambda_{11}/RT]}{x_1 v_1^L \exp - [\lambda_{11}/RT] + x_2 v_2^L \exp - [\lambda_{12}/RT]} \qquad (5.)$$

$$\psi_2 = \frac{x_2 v_2^L \exp - [\lambda_{22}/RT]}{x_2 v_2^L \exp - [\lambda_{22}/RT] + x_1 v_1^L \exp - [\lambda_{12}/RT]} \qquad (6.)$$

Then Λ_{12} and Λ_{21} are defined by the following:

$$\Lambda_{12} \equiv \frac{v_2^L}{v_1^L} \exp - [(\lambda_{12} - \lambda_{11})/RT] \qquad (7.)$$

$$\Lambda_{21} = \frac{v_1^L}{v_2^L} \exp - [(\lambda_{12} - \lambda_{22})/RT] \qquad (8.)$$

If ψ_1 and ψ_2 are substituted for ϕ_1 and ϕ_2 in the Flory-Huggins equation, the result is the Wilson equation for the excess Gibbs energy of a binary solution. This is given by the following:

$$\frac{g^E}{RT} = -x_1 \ln (x_1 + \Lambda_{12} x_2) - x_2 \ln (\Lambda_{21} x_1 + x_2) \qquad (9.)$$

If equation (9) is generalized it appears as follows:

$$\frac{g^E}{RT} = - \sum_{i=1}^{N} x_i \ln \left[\sum_{j=1}^{N} x_j \Lambda_{ij} \right] \qquad (10.)$$

with

$$\Lambda_{ij} \equiv \frac{v_j^L}{v_i^L} \exp - [(\lambda_{ij} - \lambda_{ii})/RT]$$

$$\Lambda_{ji} \equiv \frac{v_i^L}{v_j^L} \exp - [(\lambda_{ji} - \lambda_{jj})/RT]$$

The quantity g^E, the excess Gibbs energy, can be written as a function of the liquid composition at constant temperature and pressure. From this function the activity coefficient γ_k for any component k can be found by the following:

$$RT \ln \gamma_k = \left(\frac{\partial n_T \, g^E}{\partial n_K} \right)_{T,P, \text{ all } n_i \ (i \neq K)} \qquad (11.)$$

Where n_i = number of moles of component i

n_T = number of moles (total)

If equation (10) is substituted into equation (11), for any component k the result is:

$$\ln \gamma_K = - \ln \left[\sum_{j=1}^{N} x_j \Lambda_{kj} \right] + 1 - \sum_{i=1}^{N} \frac{x_i \Lambda_{ik}}{\sum_{j=1}^{N} x_j \Lambda_{ij}} \qquad (12.)$$

For the case of a binary solution, the activity coefficients are given by

$$\ln \gamma_1 = - \ln (x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \qquad (13.)$$

$$\ln \gamma_2 = - \ln (x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \qquad (14.)$$

The above two equations are the ones to be considered in the efforts to fit liquid binary iron-base metallic systems.

FITTING PROCEDURE

As a first step it was necessary to determine what method would by used to calculate the two Wilson constants that describe a given set of experimental data. It was decided that a technique for minimizing the deviations between calculated and experimental values was the best approach for selecting a pair of Wilson constants for a given system. A decision also had to be made whether the best constants were to be based on differences between calculated and experimental activities or differences between calculated and experimental activity coefficients. Table I shows the results for calculated values of a_{Cu} in the Fe - Cu system at 1550°C. Column four was based on selecting the pair of Wilson constants that minimized $\Sigma(a_{Cu_{Calc}} - a_{Cu_{Expt}})^2$. The activities in column three were calculated from the pair of Wilson constants based on minimizing $\Sigma(\gamma_{Cu_{Calc}} - \gamma_{Cu_{Expt}})^2$. As can be seen from a comparison of experimental with calculated activities in Table I a better fit at low mole fractions of Cu is produced from selecting the Wilson constant pair based on $\Sigma(\gamma_{Cu_{Calc}} - \gamma_{Cu_{Expt}})^2$. From a practical metallurgical point of view for iron-base liquid systems, low mole fractions of alloying elements are the region of most interest. With this fact as an important consideration, itwas decided to base calculation of the Wilson constants on minimizing deviations of activity coefficients.

Once the course of action had been decided, a computer program to perform the selection of Wilson constants and calculate activity

coefficients was prepared. The computer program that was developed is shown in the Appendix. The operation of the program is fairly straight forward. The approach is a trial-and-error one where a pair of Wilson constants is selected and activity coefficients are calculated by means of the Wilson equation at mole fraction values corresponding to experimental mole fraction values. The deviations between calculated and experimental activity coefficients are determined. These values are squared, summed, and stored. A new pair of Wilson constants is chosen and the process is repeated. When the selected number of pairs of Wilson constants have been tested, the summed deviations that were stored are printed out to produce a data map. From visual observation of the data map the pair of Wilson constants producing the minimum $\Sigma(\gamma_{Calc}-\gamma_{Expt})^2$, hence the best fit, can be determined. After a minimum point or area on the data map has been determined, the size of the increments between the selected Wilson constants can be reduced and the whole minimizing process repeated. To obtain Wilson constants accurate to the hundredths place, usually four passes through the program were necessary. More detailed considerations of the program are given in the Appendix.

LITERATURE DATA

Experimental activity data for seven liquid binary iron-base alloy systems were found in the literature. These systems were Fe - Si [7], Fe - Al [8], Fe - Ni [9],[10], [11], Fe - Cr [12], Fe - Mn [13], Fe - Co[11], and Fe - Cu [14]. The Fe - Si and Fe - Al systems exhibit strong negative deviations from Raoult's law. Fe - Ni, Fe - Mn, Fe - Cr and Fe - Co, on the other hand, show only slight deviations from the ideal case. Strong positive deviations are exhibited by the Fe - Cu system. It was felt that the variety of deviations exhibited by these systems would be a good test of the Wilson equation's ability to describe various types of activity behavior.

The data as presented in the literature appear in Tables II through X and also appear on the activity versus mole fraction graphs in Figures 1 through 10. In most cases the data for the systems selected were used as presented in the literature. Three sets of Fe - Ni data were fit separately by the Wilson equation. The Speiser and Belton-Fruehan Fe - Ni data sets were taken directly from the literature, but the Morris - Zellars activities were calculated from the vapor pressure data that were presented in the literature. The Fe - Cr data had been referenced to the liquid state, and these were the data used. For the Fe - Co data of Belton - Fruehan activities were recalculated from the ion current ratios. This recalculation was required to obtain a more realistic fit of the experimental data than was presented in the literature.

From ion current ratio data, which are presented in Table IX, ratios of activity coefficients were calculated with the aid of the following relation:

$$\ln\left(\frac{I_2^+}{I_1^+}\right) - \ln\left(\frac{x_2}{x_1}\right) = \ln\left(\frac{\gamma_2}{\gamma_1}\right) + C \quad (15.)$$

By selecting values of C, the $\frac{\gamma_2}{\gamma_1}$ ratio values could be fitted by the Wilson equation. Successive values of C were tried until the deviations between the γ_{Co}/γ_{Fe} values procuced by the Wilson fit and γ_{Co}/γ_{Fe} values calculated by Eq. (15) were a minimum. The ratios calculated from the Wilson equation and the ones determined from literature values are shown in Figure 8. The pair of Wilson constants that produced this fit of the literature data for Fe - Co are the values presented as describing the Fe - Co system.

For Fe - Cr, Fe - Mn, and Fe - Cu only activity data for the non-ferrous component are presented. This is the case because the experimenters for these systems had determined the activity of only the non-ferrous component.

RESULTS OF WILSON FIT

For each of the systems investigated, activity and activity coefficient values were calculated at mole fractions corresponding to the mole fraction values of the experimental data described in the literature. These activity and activity coefficient values produced by the Wilson equation, and the two Wilson constants for each of the systems determined by the minimization procedure described previously are presented in

Tables II through X. Graphically, the literature values of the activities and activity lines as calculated by the Wilson equation for each of these systems are presented in Figures 1 through 7 and Figure 10. Figure 9 presents the Wilson equations for the Fe - Co system, but as explained previously the literature data are presented in Figure 8.

From observation of the graphical results it can be observed that the Wilson equation produces a more than satisfactory fit of the systems tested. Even the crossover from positive to negative deviations from Raoult's law by the activity of iron in the Fe - Co system was generated by the Wilson equation. This crossover had been mentioned by Belton and Freuhan in their article.

In order to obtain a quantitative measure of how good the Wilson equation fit the experimental data, the root-mean-square deviations of the Wilson activities as compared to literature activity values were calculated. These values were determined from the following relation:

$$\text{RMS DEVIATION} = \sqrt{\frac{\sum_{i=1}^{N} (\gamma_{Expt} - \gamma_{Calc})^2}{N}}$$

For the systems where activity values for both components were presented two root-mean-square deviations are shown, one for the activity coefficients of the ferrous component and one for the activity coefficients of the non-ferrous component. When only activity data for the non-ferrous component had been presented in the literature, only one root-mean-square deviation for the non-ferrous activity coefficient deviations appears. In Table XII root-mean-square deviations of the calculated Wilson activity coefficients from literature activity coefficient values are summarized.

As an overall look at the seven systems whose activities have been described by the Wilson equation, the Wilson constants for these systems have been plotted on Λ_{21} versus Λ_{12} graphs in Figures 11 and 12. Also shown in Figure 11 are three curves, each at an indicated mole fraction of component 1, which express the values of the Wilson constant pairs when ideal solution behavior is obeyed. That is to say, if γ_1 in the one Wilson equation is set equal to unity and the mole fraction values of x_1 are set at 0.05, 0.5, and 0.95 as indicated, the behavior of Λ_{21}, as Λ_{12} varies, is as indicated. The region enclosed by these curves is a transitional region. If the pair of Wilson constants describing a particular system falls within this region, the activity of the system described will be close to the ideal case and the activity curve may cross the Raoult's law line. In these figures systems having constants which lie to the southwest of this region exhibit positive deviations from ideality, and constants lying to the northeast of the transition region are indicative of systems having negative deviations from ideality.

In Figure 12 the curves shown represent Wilson constant pairs at the indicated mole fraction values when γ_2 obeys ideality. These values were obtained by setting γ_2 equal to unity in the second Wilson equation, fixing x_1 at 0.05, 0.5, and 0.95 respectively, and determining Λ_{21} as Λ_{12} is varied.

These two graphs serve as an excellent method of comparing the relative deviations from ideality of the systems investigated and offer

a means of predicting deviations in activity from ideality based solely on the value of the pair of Wilson constants. Consider the seven systems that have been discussed. Both ferrous and non-ferrous components of the Fe - Si and Fe - Al systems exhibit large negative deviations from ideality. It can be seen that the positions of the pair of Wilson constants for these systems in Figures 11 and 12 are far removed from the transition region. The position of the Wilson constant pair for the Fe - Ni system nearer to the transition region indicates that both iron and nickel exhibit slight negative deviations. This slight negative deviation is verified by each of the three sets of Fe - Ni data studied. From the location of the Wilson constants for the Fe - Cr system, the Cr activities should exhibit only slight negative deviations. This is the case. From Figure 11 it can be observed that the activity of Fe will also exhibit negative deviations from ideality. Wilson constants for the ferrous components of the Fe - Co and Fe - Mn systems lie in the middle of transition region in Figure 11. This position would indicate nearly ideal behavior and possible existence of a crossover from positive to negative deviations from ideality. This is the situation for Fe in the Fe - Co system; the Fe activity curve crosses the Raoult's law line at about 0.5 mole fraction Co. There are no experimental data in the literature for the activity of Fe in the Fe - Mn system, but from the position of the pair of Wilson constants it is fair to predict that the activities of Fe will also exhibit both positive and negative deviations. The non-ferrous components of these two systems lie on the positive edge of

the transition region, and activity values verify this behavior. Finally, for the Fe - Cu system, Wilson constant pairs lie well to the left of the region of ideality confirming positive deviation of Cu activities and predicting positive deviations for the activity of Fe in the Fe - Cu system.

DISCUSSION OF RESULTS

Darken's Formalism

Darken [1], [15] has made the most comprehensive attempt, which has appeared in the literature to date, to formalize the behavior of activities in liquid binary iron-base systems. In Darken's approach the entire range of concentrations is divided into three regions. These are two terminal regions and a central region which must be arbitrarily located. The width of either of the terminal regions has been found to vary from 0.15 to 0.50 atom fraction.

The terminal regions are determined by observation of straight line sections when experimental data are plotted on a $\log\gamma_1$, versus $(1-x_1)^2$ graph. Mathematically these regions are expressed by the following:

$$\log \gamma_1 = \alpha x_2^2 \qquad (16)$$

or

$$\log \gamma_2 = \alpha' x_1^2 \qquad (17)$$

These expressions can represent departures from Raoult's law up to considerable solute concentrations. If the solvent is expressed by Eq. (16.), for example, then using the Gibbs-Duhem equation,

$$x_1 \, d \log \gamma_1 + x_2 \, d \log \gamma_2 = 0 \qquad (18)$$

the activity coefficient of the solute must be represented by:

$$\log \gamma_2 = \alpha x_1^2 + I \qquad (19)$$

If equations (16.) and (19.) held over the entire range of compositions, then I would be equal to zero. Such is not the case because these relations are only applied to a part of the concentration range;

therefore, I does not equal zero. It then becomes necessary to evaluate the constant I in Eq. (19.). This constant can be evaluated when α is known and the point at which the straight line region intercepts the log γ_2 axis can be observed. This intercept at $x_1 = 1$ is designated as log γ_2°. Darken determined the α values by measuring the slopes of the straight line regions on the appropriate ends of the concentration range. The convention followed for subscripts for the α values is to name the solvent first and the solute second. In the central, or transition region of compositions, Darken's formalism requires that the two terminal straight line regions be joined by an arbitrarily drawn curve.

For comparison of activity values calculated by the Wilson equation with activities produced by Darken's formalism, it was necessary to calculate activity coefficients by Darken's method. In the literature to date Darken has presented values of the four constants necessary to calculate activity coefficients for five of the seven systems investigated. He has presented two separate sets of constants for the Fe - Ni system. One fits the Belton and Fruehan data, while the second applies to the combined Speiser and Morris - Zellars sets of data. Therefore, two sets of Fe - Ni data based on Darken's formalism will be presented. The only systems not considered by Darken are the Fe - Co and Fe - Cr alloys. The values of the four Darken parameters for each system studied are presented in Table XI.

Activity coefficients calculated by Darken's formalism along with

the corresponding activities are presented in Tables II through VI, VIII, and X. These activity coefficients produced by Darken's formalism were calculated at mole fraction values corresponding to the mole fractions at which the Wilson and literature activities are presented. This was done to allow comparison of the resulting activity coefficient and activity values.

As was done for the values calculated by the Wilson equation, values of root-mean-square deviations of activity coefficients determined by Darken's formalism compared to experimental values of activity coefficients are presented. The values appear beside the root-mean-square deviations for the Wilson activity coefficients in Table XII.

Comparison of Wilson and Darken Approaches

As can be seen by comparing root-mean-square deviation values in Table XII, the formalism presented by Darken produces a slightly better fit than the Wilson equation. There are several considerations other than root-mean-square deviations that should be considered before one can choose between the two approaches. The first is that Darken's procedure for selection of the terminal regions is quite arbitrary. Secondly, the equations and the calculations that must be made for determination of activity coefficients of both components across the whole composition range are complicated and somewhat confusing. This confusion is caused by the need to use two equations

and a transition or estimation region for each of the system's two components. Also, four constants must be determined.

On the other hand the Wilson equation method of determining activity coefficients involves only two equations. One describes the activity coefficients of one of the components over the entire range of compositions, while the other equation describes the activity coefficient behavior of the second component over the entire composition region. Only two constants, which are the same for each of the equations mentioned above, are necessary to compute activity coefficient behavior. There are no composition regions in which behavior must be estimated by eye. It has been clearly demonstrated that the Wilson equation is capable of expressing all degrees of deviation from ideal solution behavior. Therefore, when an overall approach for expressing activity coefficients in liquid binary iron-base alloys is desired, the Wilson equation must be considered both practical and quantitatively acceptable.

CONCLUSIONS

As a result of the work conducted, several conclusions can be made:

1. The Wilson equation is capable of accurately describing activity coefficient behavior of liquid binary iron-base alloys. These alloys exhibit a wide range of behavior from strong positive deviations from Raoult's Law to strong negative deviations, including systems with only slight deviations from Raoult's Law and those which exhibit both positive and negative deviations in the same system.
2. The optimum Wilson constants can be determined by relatively simple computer techniques which are rather economical in both user and machine time.
3. The fit obtained is almost as good as that produced by Darken's approach, with the added benefit that the arbitrariness and need for four constants dictated by Darken is replaced by a single equation that contains only two constants and covers the complete composition range.

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TABLE I Results of Alternative Minimizing Techniques

x_{cu}	EXPT a_{cu}	MINIMIZING $\Sigma(\gamma_{Cu}^{Calc} - \gamma_{Cu}^{Expt})^2$ a_{cu}	MINIMIZING $\Sigma(a_{Cu}^{Calc} - a_{Cu}^{Expt})^2$ a_{cu}
0.0265	0.216	0.2194	0.2257
0.0442	0.325	0.3277	0.3327
0.061	0.424	0.4104	0.4122
0.088	0.521	0.5132	0.5084
0.142	0.660	0.6473	0.6294
0.171	0.687	0.6948	0.6710
0.217	0.729	0.7491	0.7179
0.328	0.786	0.8216	0.7807
0.467	0.821	0.8628	0.8196
0.626	0.870	0.8881	0.8504
0.792	0.888	0.9130	0.8886
0.883	0.923	0.9348	0.9216

TABLE II Fe - Si ACTIVITY DATA

DATA SOURCE: Hsu, Polyakov, and Samarin(7.)
PERTINENT INFORMATION : TEMP 1600°C
CALCULATED WILSON CONSTANTS: $\Lambda_{Si-Fe}=2.62$, $\Lambda_{Fe-Si}=7.32$

LITERATURE DATA			WILSON EQ.		DARKEN FORMALISM	
x_{Si}	γ_{Si}	a_{Si}	γ_{Si}	a_{Si}	γ_{Si}	a_{Si}
0.338	0.169	0.057	0.238	0.080	0.098	0.0331
0.460	0.274	0.126	0.412	0.190	0.279	0.128
0.565	0.577	0.326	0.570	0.322	0.580	0.328
0.654	0.798	0.522	0.699	0.457	0.785	0.513
0.730	0.893	0.652	0.800	0.584	0.877	0.640
0.774	0.926	0.717	0.853	0.660	0.912	0.706
0.812	0.927	0.753	0.893	0.725	0.939	0.762
0.853	0.954	0.814	0.932	0.795	0.963	0.821
0.856	0.956	0.818	0.934	0.800	0.964	0.825
0.882	0.972	0.857	0.954	0.842	0.976	0.861
0.941	0.993	0.934	0.988	0.929	0.994	0.935
0.980	1.005	0.985	0.998	0.979	0.999	0.979
0.988	1.002	0.990	0.999	0.988	0.999	0.987
x_{Fe}	γ_{Fe}	a_{Si}	γ_{Si}	a_{Si}	γ_{Si}	a_{Si}
0.270	0.0885	0.0239	0.122	0.033	0.053	0.0143
0.346	0.0908	0.0314	0.165	0.057	0.064	0.0221
0.435	0.0936	0.0407	0.227	0.099	0.078	0.0339
0.540	0.191	0.103	0.319	0.172	0.221	0.119
0.662	0.467	0.309	0.458	0.303	0.442	0.293
0.794	0.734	0.583	0.660	0.524	0.740	0.588
0.825	0.790	0.652	0.717	0.591	0.804	0.663
0.861	0.857	0.738	0.786	0.677	0.871	0.750
0.896	0.913	0.818	0.855	0.766	0.926	0.830
0.919	0.950	0.873	0.899	0.826	0.954	0.877
0.946	0.957	0.905	0.947	0.896	0.979	0.926
0.975	0.992	0.967	0.986	0.961	0.996	0.971
0.990	1.000	0.990	0.998	0.988	0.999	0.989

TABLE III Fe - Al ACTIVITY DATA

DATA SOURCE: BELTON and FRUEHAN (8.)
PERTINENT INFORMATION: TEMP 1600°C
CALCULATED WILSON CONSTANTS: $\Lambda_{Al-Fe} = 1.98$, $\Lambda_{Fe-Al} = 4.41$

	LITERATURE DATA		WILSON EQ.		DARKEN FORMALISM	
x_{Al}	γ_{Al}	a_{Al}	γ_{Al}	a_{Al}	γ_{Al}	a_{Al}
0.1	0.064	0.006	0.071	0.007	0.063	0.0063
0.2	0.151	0.030	0.167	0.033	0.150	0.03 00
0.3	0.324	0.095	0.293	0.088	0.295	0.0885
0.4	0.445	0.178	0.434	0.174	0.444	0.178
0.5	0.572	0.286	0.577	0.289	0.569	0.284
0.6	0.699	0.419	0.711	0.427	0.697	0.418
0.7	0.817	0.572	0.828	0.579	0.816	0.571
0.8	0.913	0.730	0.919	0.735	0.914	0.731
0.9	0.983	0.885	0.979	0.881	0.978	0.880
x_{Fe}	γ_{Fe}	a_{Fe}	γ_{Fe}	a_{Fe}	γ_{Fe}	a_{Fe}
0.1	0.127	0.013	0.129	0.013	0.125	0.012
0.2	0.183	0.037	0.184	0.037	0.183	0.037
0.3	0.249	0.075	0.252	0.076	0.257	0.077
0.4	0.340	0.136	0.333	0.133	0.344	0.138
0.5	0.441	0.220	0.430	0.215	0.442	0.221
0.6	0.538	0.328	0.542	0.325	0.547	0.328
0.7	0.635	0.445	0.668	0.468	0.673	0.471
0.8	0.817	0.654	0.804	0.644	0.816	0.653
0.9	0.958	0.862	0.933	0.839	0.950	0.855

TABLE IV Fe - Ni ACTIVITY DATA

DATA SOURCE: Zellars and co-workers[9.]
PERTINENT INFORMATION: TEMP 1600°C
CALCULATED WILSON CONSTANTS: Λ_{Ni-Fe} = 3.313, Λ_{Fe-Ni} = 0.302

LITERATURE DATA		WILSON EQ.		DARKEN FORMALISM		
x_{Ni}	γ_{Ni}	a_{Ni}	γ_{Ni}	a_{Ni}	γ_{Ni}	a_{Ni}
0.1006	0.646	0.065	0.638	0.064	0.672	0.068
0.1203	0.690	0.083	0.644	0.078	0.674	0.081
0.1593	0.691	0.110	0.657	0.105	0.679	0.108
0.1980	0.667	0.132	0.671	0.133	0.683	0.135
0.2400	0.658	0.158	0.686	0.165	0.687	0.165
0.3482	0.672	0.234	0.727	0.253	0.697	0.243
0.4082	0.740	0.302	0.752	0.307	0.702	0.287
0.4873	0.745	0.363	0.787	0.384	0.735	0.358
0.5677	0.787	0.447	0.824	0.468	0.793	0.450
0.6382	0.862	0.550	0.858	0.548	0.850	0.542
0.7426	0.910	0.673	0.910	0.676	0.921	0.684
0.8435	0.964	0.813	0.958	0.808	0.970	0.818
0.8940	1.020	0.912	0.978	0.874	0.986	0.882

x_{Fe}	γ_{Fe}	a_{Fe}	γ_{Fe}	a_{Fe}	γ_{Fe}	a_{Fe}
0.1056	0.521	0.055	0.505	0.053	0.510	0.054
0.1997	0.646	0.129	0.639	0.128	0.622	0.124
0.2573	0.738	0.190	0.707	0.182	0.695	0.179
0.3126	0.733	0.229	0.764	0.239	0.767	0.240
0.3618	0.763	0.276	0.807	0.292	0.834	0.302
0.4323	0.921	0.398	0.859	0.371	0.925	0.400
0.5124	0.935	0.479	0.905	0.464	0.978	0.501
0.5918	0.995	0.589	0.939	0.556	0.985	0.583
0.6534	0.966	0.631	0.959	0.626	0.989	0.646
0.7590	1.022	0.776	0.982	0.745	0.995	0.755
0.8797	0.990	0.871	0.996	0.876	0.999	0.879
0.8994	1.062	0.955	0.997	0.897	0.999	0.898

TABLE V Fe - Ni ACTIVITY DATA

DATA SOURCE: Speiser and co-workers (10.)
PERTINENT INFORMATION: TEMP 1600 °C
CALCULATED WILSON CONSTANTS: $\Lambda_{Ni-Fe} = 3.54$, $\Lambda_{Fe-Ni} = 0.28$

	LITERATURE DATA		WILSON EQ.		DARKEN FORMALISM	
x_{Ni}	γ_{Ni}	a_{Ni}	γ_{Ni}	a_{Ni}	γ_{Ni}	a_{Ni}
0.1	0.700	0.07	0.612	0.061	0.673	0.067
0.2	0.700	0.14	0.646	0.129	0.683	0.137
0.3	0.700	0.21	0.684	0.205	0.692	0.208
0.4	0.700	0.28	0.726	0.290	0.701	0.280
0.5	0.740	0.37	0.772	0.386	0.743	0.372
0.6	0.767	0.46	0.822	0.493	0.820	0.492
0.7	0.843	0.59	0.875	0.612	0.894	0.626
0.8	0.950	0.76	0.929	0.743	0.952	0.762
0.9	0.989	0.89	0.977	0.879	0.988	0.889
x_{Fe}	γ_{Fe}	a_{Fe}	γ_{Fe}	a_{Fe}	γ_{Fe}	a_{Fe}
0.1	0.400	0.04	0.458	0.046	0.505	0.050
0.2	0.550	0.11	0.612	0.122	0.622	0.124
0.3	0.767	0.23	0.733	0.220	0.750	0.225
0.4	0.900	0.36	0.825	0.330	0.885	0.354
0.5	0.960	0.48	0.892	0.446	0.977	0.489
0.6	0.983	0.59	0.938	0.563	0.985	0.591
0.7	0.986	0.69	0.969	0.678	0.992	0.694
0.8	0.988	0.79	0.987	0.790	0.996	0.792
0.9	1.000	0.90	0.997	0.897	0.999	0.899

TABLE VI Fe - Ni ACTIVITY DATA

DATA SOURCE: Belton and Fruehan[11.]
PERTINENT INFORMATION: TEMP 1600 ℃
CALCULATED WILSON CONSTANTS: Λ_{Ni-Fe}= 3.27, Λ_{Fe-Ni}= 0.28

	LITERATURE DATA		WILSON EQ.		DARKEN FORMALISM	
x_{Ni}	γ_{Ni}	a_{Ni}	γ_{Ni}	a_{Ni}	γ_{Ni}	a_{Ni}
0.1	0.725	0.073	0.659	0.066	0.717	0.072
0.2	0.733	0.142	0.692	0.139	0.726	0.145
0.3	0.742	0.222	0.728	0.218	0.733	0.220
0.4	0.751	0.300	0.767	0.307	0.740	0.296
0.5	0.774	0.387	0.809	0.405	0.761	0.380
0.6	0.821	0.493	0.854	0.512	0.817	0.490
0.7	0.894	0.626	0.900	0.630	0.892	0.624
0.8	0.952	0.762	0.945	0.756	0.951	0.761
0.9	0.988	0.889	0.982	0.884	0.987	0.888
x_{Fe}	γ_{Fe}	a_{Fe}	γ_{Fe}	a_{Fe}	γ_{Fe}	a_{Fe}
0.1	0.503	0.050	0.528	0.053	0.506	0.051
0.2	0.622	0.124	0.662	0.132	0.628	0.126
0.3	0.750	0.225	0.767	0.230	0.759	0.228
0.4	0.877	0.351	0.846	0.338	0.895	0.358
0.5	0.958	0.479	0.904	0.452	0.960	0.480
0.6	0.988	0.593	0.945	0.567	0.989	0.593
0.7	0.993	0.695	0.972	0.680	0.994	0.696
0.8	0.997	0.798	0.989	0.791	0.997	0.726
0.9	0.999	0.899	0.997	0.898	0.999	0.899

TABLE VII Fe - Cr ACTIVITY DATA

DATA SOURCE: Fruehan (12.)

PERTINENT INFORMATION :
1. DATA PRESENTED ENDS AT THE SOLUBILITY LIMIT
2. DATA : REFERENCED TO THE PURE LIQUID AS THE STD. STATE
3. TEMP 1600°C

CALCULATED WILSON CONSTANTS: $\Lambda_{Cr-Fe} = 3.19$, $\Lambda_{Fe-Cr} = 0.15$

LITERATURE DATA			WILSON EQUATION	
x_{Cr}	γ_{Cr}	a_{Cr}	γ_{Cr}	a_{Cr}
0.115	0.799	0.092	0.768	0.088
0.144	0.682	0.098	0.777	0.112
0.167	0.810	0.135	0.784	0.131
0.187	0.846	0.158	0.791	0.148
0.212	0.792	0.167	0.799	0.169
0.324	0.766	0.248	0.836	0.271
0.351	0.869	0.305	0.845	0.297
0.380	0.847	0.322	0.855	0.325
0.405	0.928	0.375	0.864	0.350
0.482	0.905	0.436	0.891	0.429
0.522	0.865	0.452	0.905	0.472

TABLE VIII Fe - Mn ACTIVITY DATA

DATA SOURCE: Sanbangi and Ohtani (13.)
PERTINENT INFORMATION: TEMP 1600 °C
CALCULATED WILSON CONSTANTS: Λ_{Mn-Fe} = 2.75, Λ_{Fe-Mn} = 0.00

LITERATURE DATA			WILSON EQ.		DARKEN FORMALISM	
x_{Mn}	γ_{Mn}	a_{Mn}	γ_{Mn}	a_{Mn}	γ_{Mn}	a_{Mn}
0.004	1.500	0.006	1.004	0.004	1.257	0.005
0.012	1.833	0.022	1.012	0.012	1.252	0.015
0.013	1.308	0.017	1.012	0.013	1.251	0.016
0.048	1.062	0.051	1.042	0.050	1.232	0.059
0.070	1.514	0.106	1.058	0.074	1.221	0.086
0.079	0.848	0.067	1.063	0.084	1.215	0.096
0.091	0.813	0.074	1.070	0.097	1.210	0.110
0.104	1.346	0.140	1.078	0.112	1.203	0.125
0.134	1.104	0.148	1.092	0.146	1.189	0.159
0.146	0.884	0.129	1.097	0.160	1.183	0.173
0.194	1.469	0.285	1.112	0.216	1.163	0.226
0.196	1.097	0.215	1.112	0.218	1.160	0.227
0.198	1.444	0.286	1.113	0.220	1.160	0.230
0.280	1.179	0.330	1.125	0.315	1.127	0.316
0.355	1.177	0.418	1.126	0.400	1.101	0.391
0.368	0.973	0.358	1.126	0.414	1.096	0.403
0.480	1.260	0.605	1.114	0.534	1.064	0.511
0.524	0.863	0.452	1.106	0.580	1.053	0.552
0.550	1.216	0.669	1.101	0.606	1.048	0.576
0.680	0.971	0.660	1.072	0.729	1.024	0.696
0.717	1.049	0.752	1.063	0.762	1.019	0.731
0.800	1.040	0.832	1.042	0.834	1.009	0.807

TABLE IX Fe - Co ACTIVITY DATA

DATA SOURCE: Belton and Fruehan[11.]
PERTINENT INFORMATION: TEMP 1600°C
DATA based on ion current ratios
CALCULATED WILSON CONSTANTS: $\Lambda_{Co-Fe} = 2.08$, $\Lambda_{Fe-Co} = 0.16$

LITERATURE DATA		WILSON EQUATION			
x_{Co}	$\ln(I^+_{Co}/I^+_{Fe})$	γ_{Co}/γ_{Fe}	γ_{Co}/γ_{Fe}	γ_{Co}	a_{Co}
0.058	-3.91	1.000	1.118	1.008	0.951
0.095	-3.21	1.174	1.120	1.017	0.925
0.119	-3.12	1.000	1.121	1.071	0.776
0.197	-2.41	1.128	1.124	1.097	0.660
0.299	-1.84	1.139	1.124	1.110	0.569
0.335	-1.60	1.234	1.123	1.121	0.422
0.376	-1.34	1.336	1.121	1.123	0.376
0.513	-1.07	1.000	1.100	1.123	0.336
0.602	-0.67	1.041	1.071	1.123	0.221
0.724	-0.27	0.896	0.996	1.120	0.133
0.910	0.94	0.779	0.725	1.119	0.106
0.943	1.17	0.594	0.644	1.117	0.065

x_{Fe}	γ_{Fe}	a_{Fe}
0.057	1.567	0.089
0.090	1.403	0.134
0.276	1.075	0.297
0.398	1.024	0.408
0.487	1.009	0.491
0.624	1.000	0.624
0.665	0.9995	0.665
0.701	0.9992	0.704
0.803	0.9992	0.802
0.881	0.9996	0.881
0.905	0.9998	0.905
0.942	0.9999	0.942

TABLE X Fe - Cu ACTIVITY DATA

DATA SOURCE: Morris and Zellars[14.]
PERTINENT INFORMATION: TEMP 1550° C
CALCULATED WILSON CONSTANTS: Λ_{Cu-Fe}= .239, Λ_{Fe-Cu}=.135

	LITERATURE DATA		WILSON EQ.		DARKEN FORMALISM	
x_{Cu}	γ_{Cu}	a_{Cu}	γ_{Cu}	a_{Cu}	γ_{Cu}	a_{Cu}
0.0265	8.151	0.216	8.277	0.219	8.136	0.216
0.0442	7.356	0.325	7.414	0.328	7.428	0.328
0.061	6.951	0.424	6.728	0.410	6.823	0.416
0.088	5.920	0.521	5.832	0.513	5.971	0.525
0.142	4.648	0.660	4.559	0.647	4.629	0.657
0.171	4.108	0.687	4.063	0.695	4.062	0.695
0.217	3.356	0.729	3.452	0.749	3.334	0.723
0.328	2.396	0.786	2.505	0.822	2.234	0.733
0.467	1.758	0.821	1.848	0.863	1.803	0.842
0.626	1.390	0.870	1.419	0.888	1.403	0.878
0.792	1.121	0.888	1.153	0.913	1.124	0.890
0.883	1.045	0.923	1.059	0.935	1.038	0.917

TABLE XI

Parameters for Darken's Formalism
(using Pure Liquid as the Standard State)

SYSTEM	TEMPERATURE	PARAMETERS			
		$\log \gamma_X^\circ$	α_{Fe-X}	$\log \gamma_{Fe}^\circ$	α_{X-Fe}
Fe - Si	1600 °C	-2.75	-3.10	-1.64*	-0.78
Fe - Al (Belton - Fruehan)	1600 °C	-1.62	-2.21	-1.09	-0.98
Fe - Ni (Speiser; Morris Zellars)	1600° C	-0.18	-0.04	-0.40	-0.54
Fe - Ni (Belton - Fruehan)	1600° C	-0.15	-0.03	-0.40	-0.55
Fe - Mn	1600° C	0.1	0.1	---	0.1
Fe - Cu	1550 ° C	0.971	1.158	---	1.172

* Value obtained by Integration

TABLE XII

ROOT - MEAN - SQUARE DEVIATIONS OF ACTIVITY COEFFICIENTS

SYSTEM	COMPONENT	RMS VALUES FOR WILSON FIT DATA	RMS VALUES FOR DARKEN FIT DATA
Fe - Si	Fe	0.0695	0.0194
	Si	0.0623	0.0215
Fe - Al	Fe	0.0152	0.0136
	Al	0.0129	0.0099
Fe - Ni (Morris - Zellars)	Fe	0.0387	0.0365
	Ni	0.0307	0.0212
Fe - Ni (Speiser)	Fe	0.0482	0.0436
	Ni	0.0420	0.0269
Fe - Ni (Belton - Fruehan)	Fe	0.0312	0.0071
	Ni	0.0315	0.0237
Fe - Mn	Mn	0.2874	0.2369
Fe - Cu	Cu	0.0990	0.0684

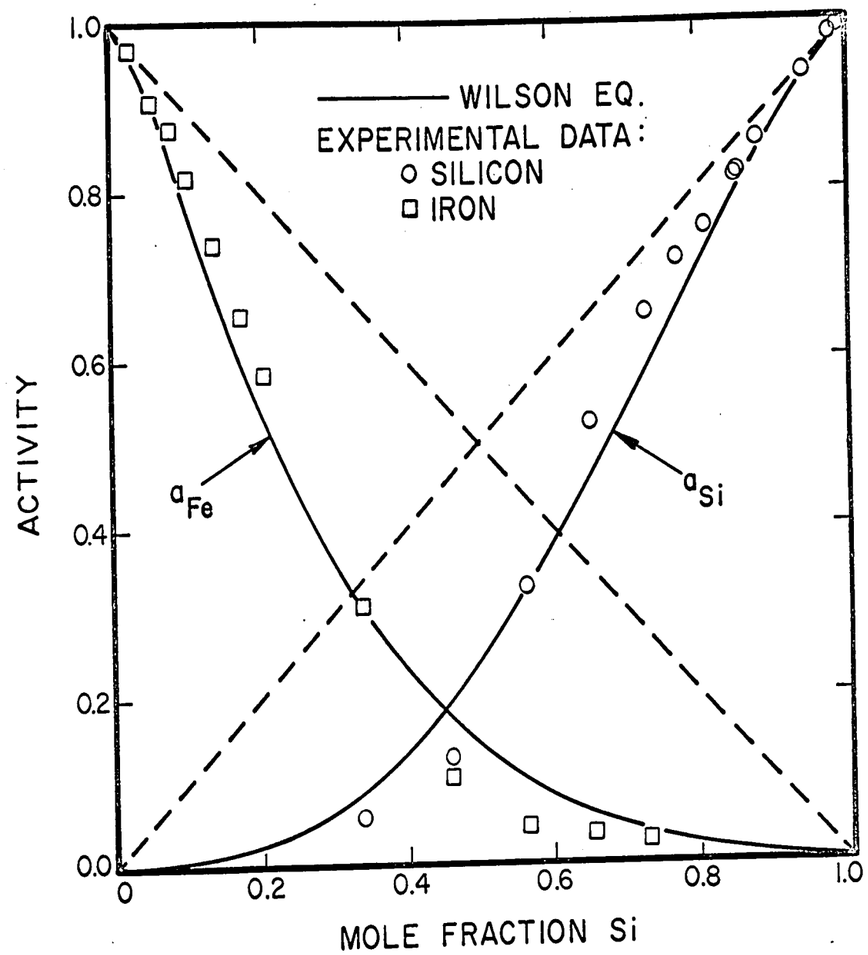

Fig.1. Activities in iron-silicon binary alloys at 1600°C. (Expt. data from Hsu, Polyakov, and Samarin[7].)

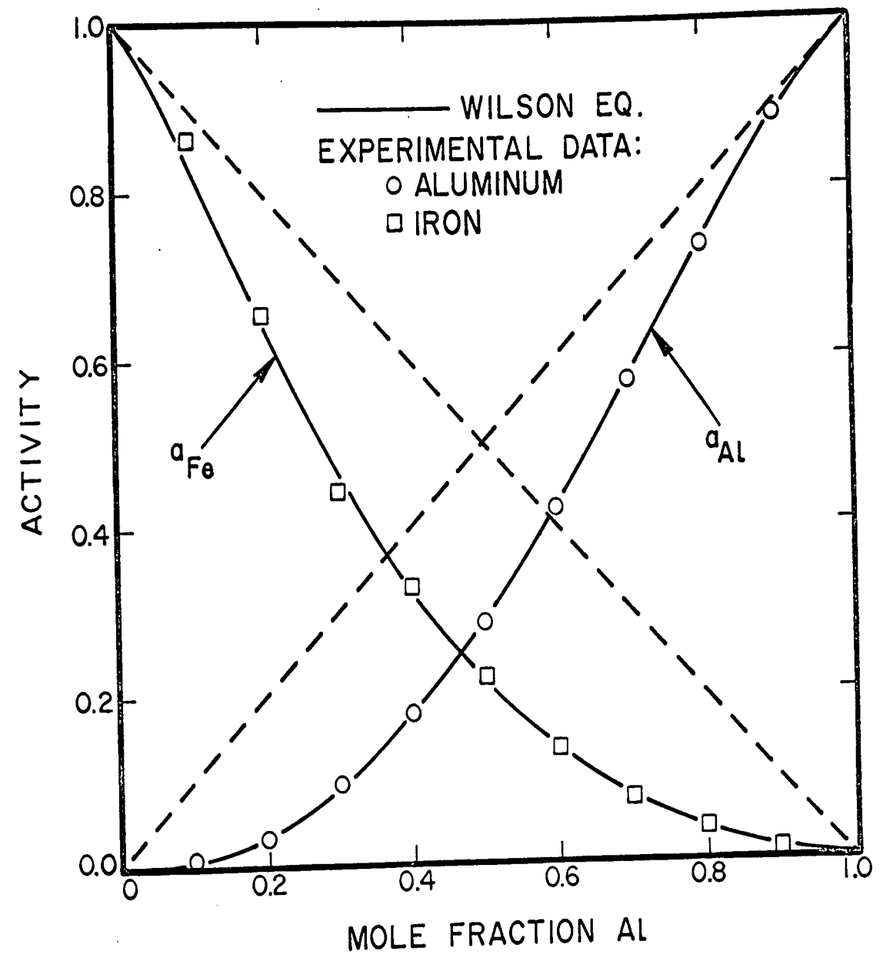

Fig.2. Activities in iron-aluminum binary alloys at 1600°C. (Expt data from Belton and Fruehan[8].)

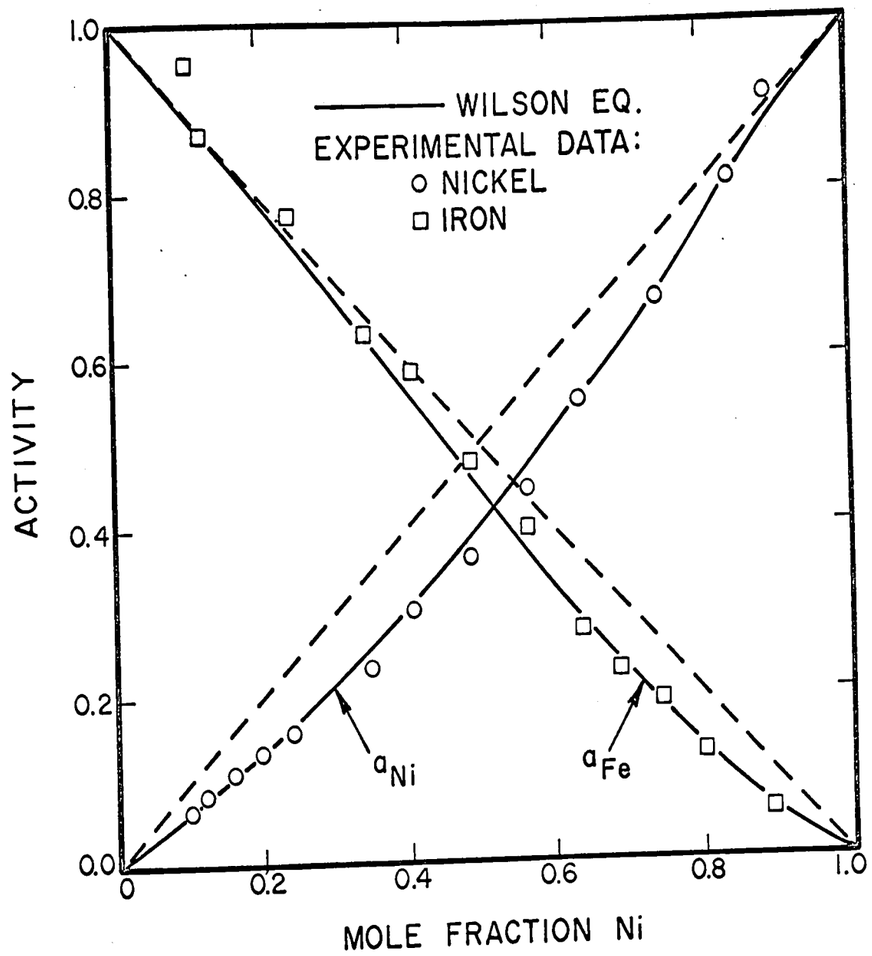

Fig.3. Activities in iron-nickel binary alloys at 1600°C. (Expt. data from Zellars et al[9].)

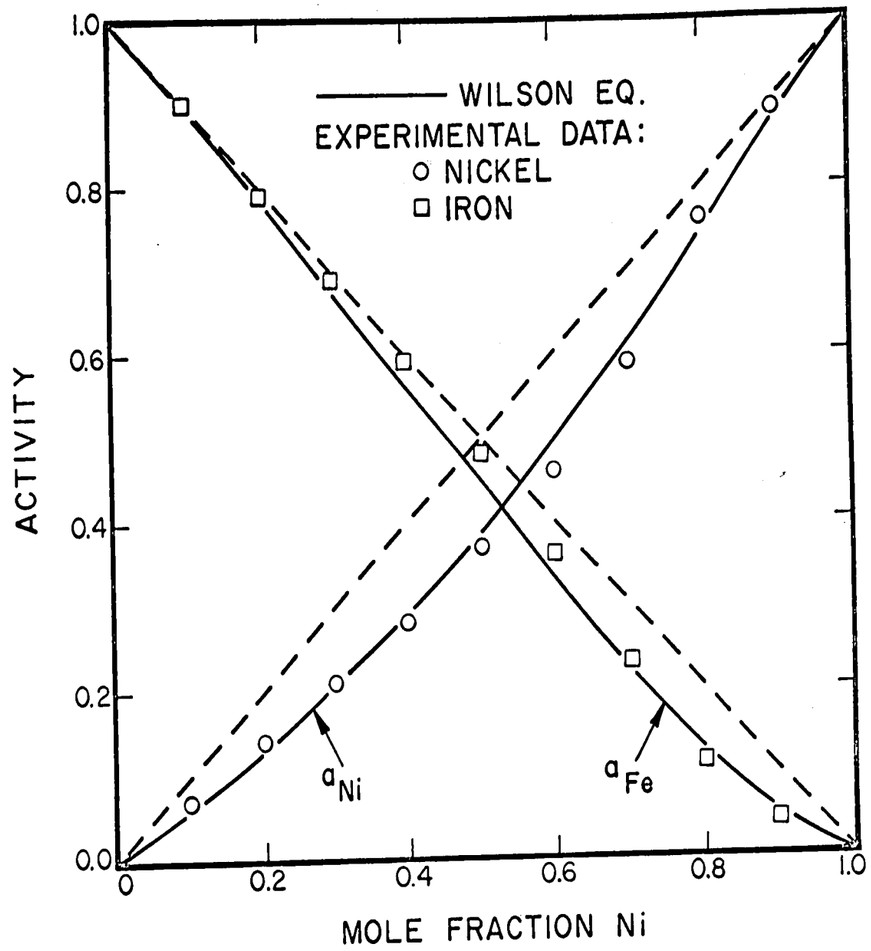

Fig.4. Activities in iron-nickel binary alloys at 1600°C. (Expt. data from Speiser et al[10].)

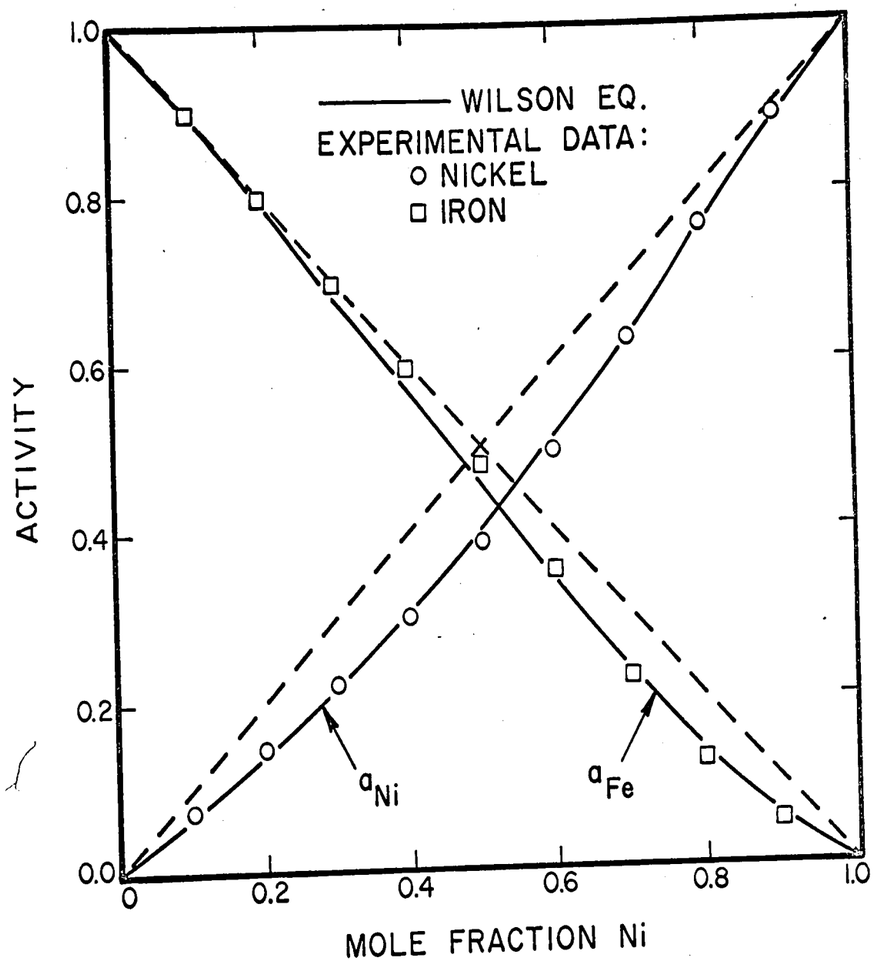

Fig.5. Activities in iron-nickel binary alloys at 1600°C. (Expt data from Belton and Fruehan[11].)

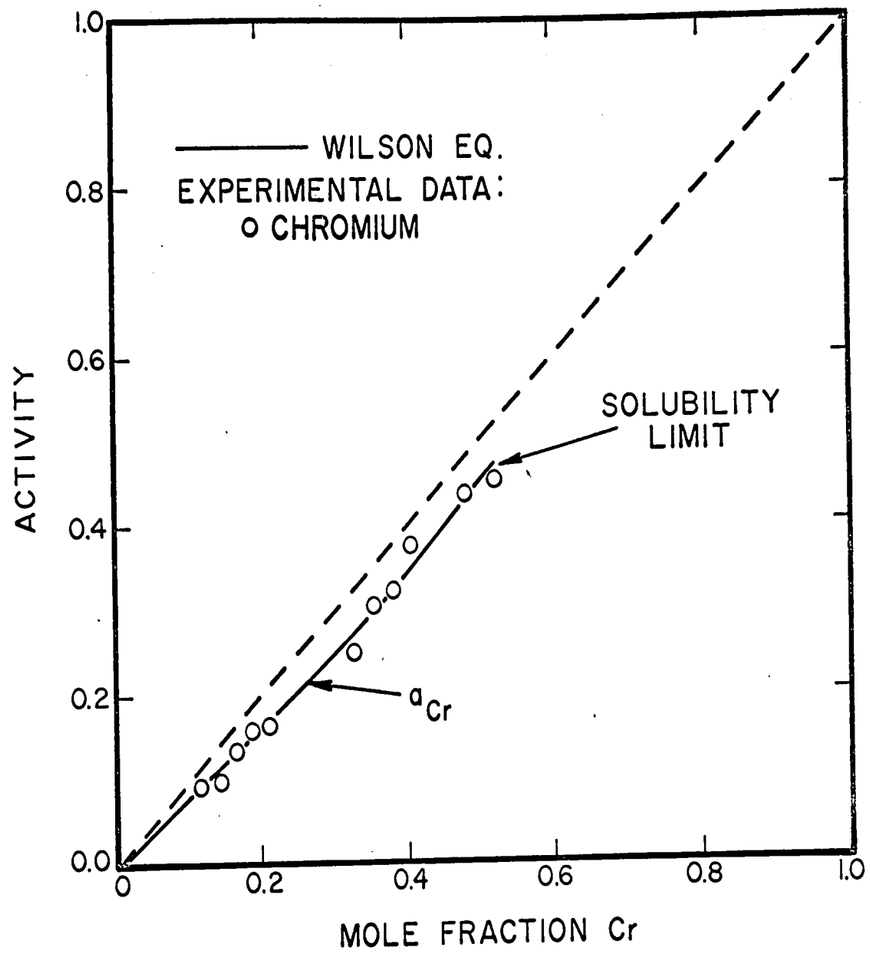

Fig.6. Activities in iron-chromium binary alloys at 1600°C. referenced to the liquid state. (Expt data from Fruehan[12].)

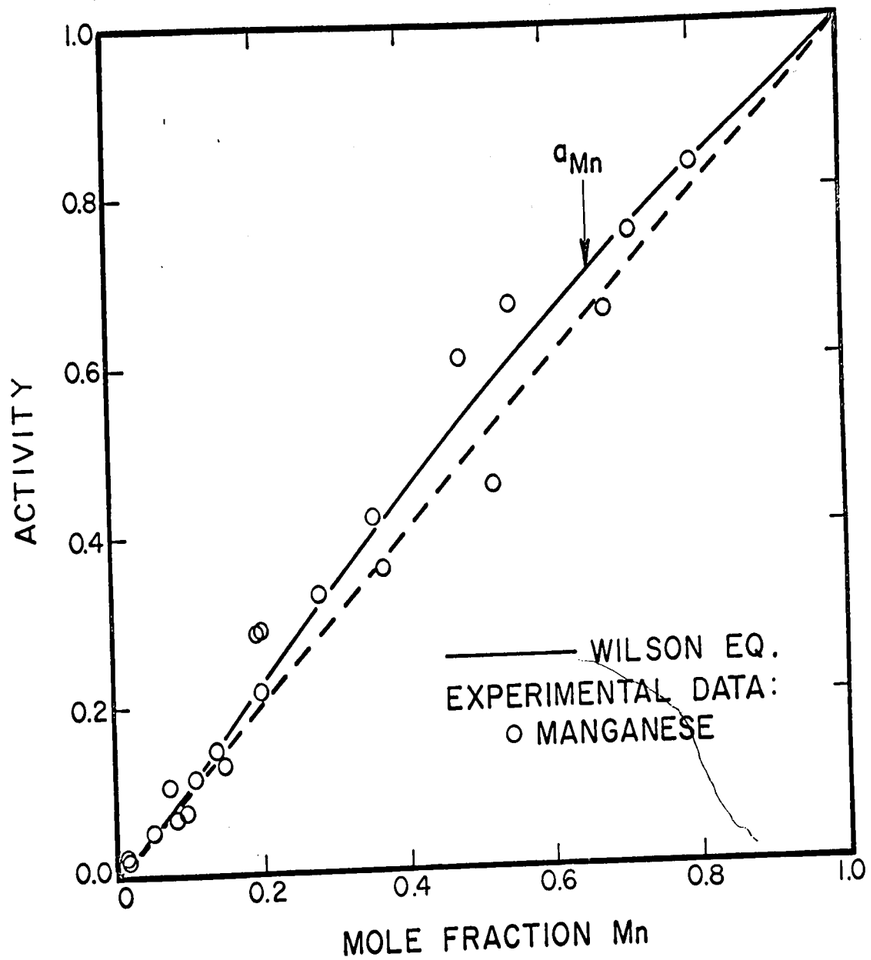

Fig.7. Activities in iron-manganese binary alloys at 1600°C. (Expt data from Sanbongi and Ohtani[13].)

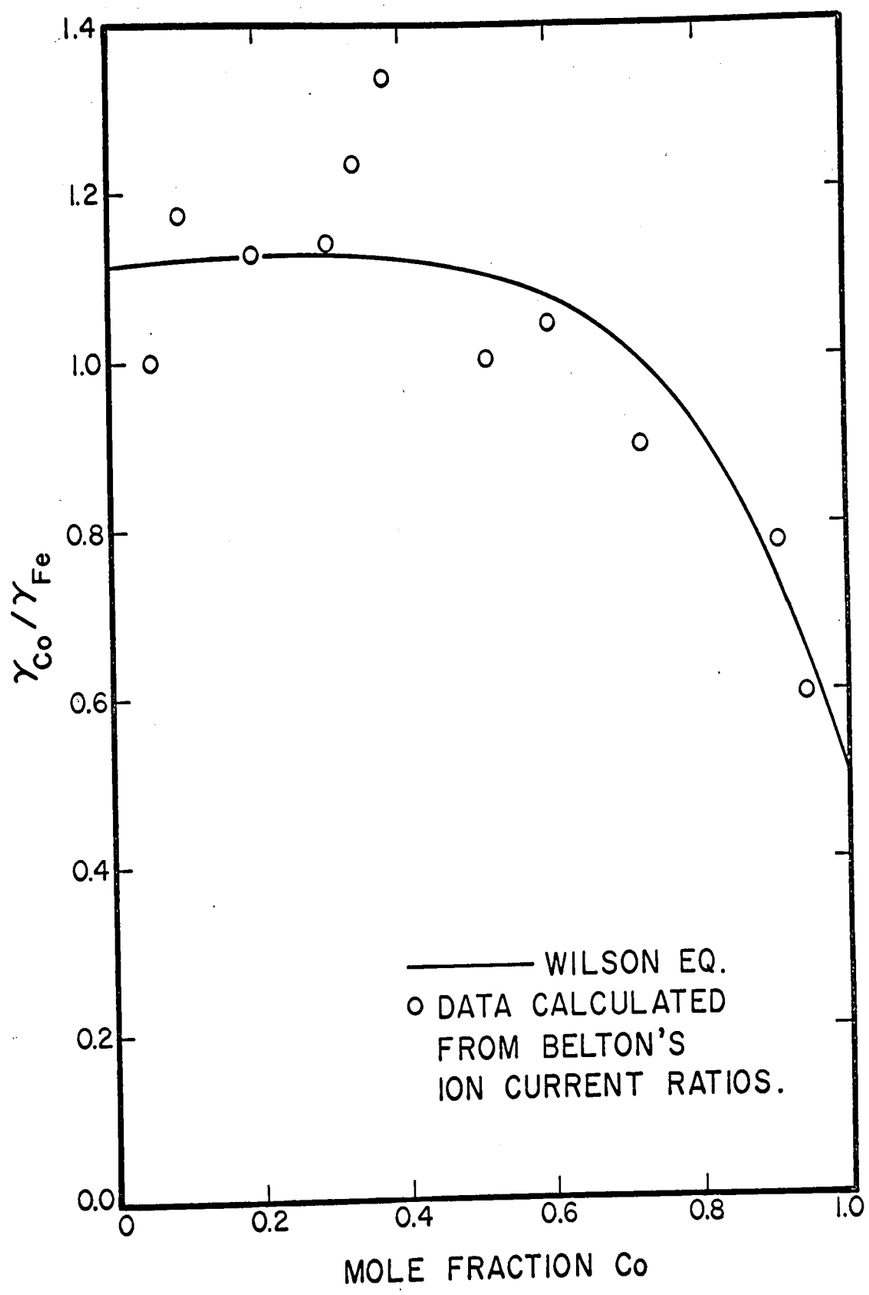

Fig.8. Activity coefficient ratios in binary iron-cobalt alloys at 1590°C. (Data presented is based on Belton-Fruehan ion current ratios[11])

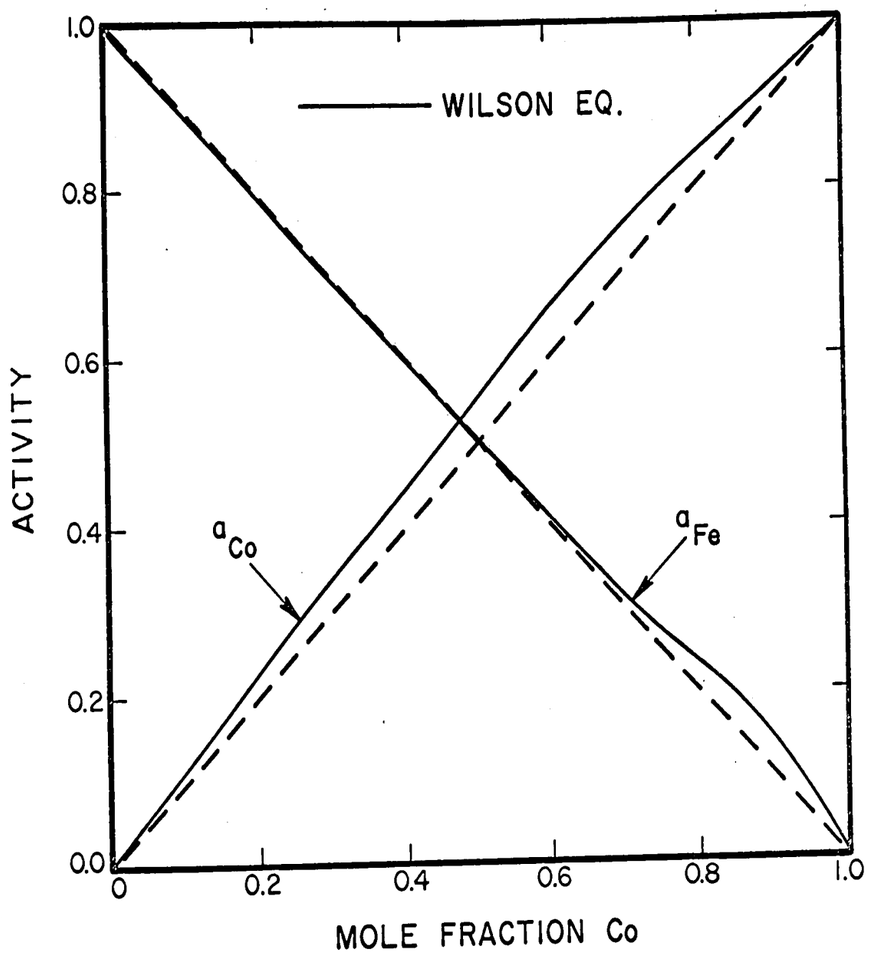

Fig.9. Activities in iron-cobalt binary alloys at 1590°C.

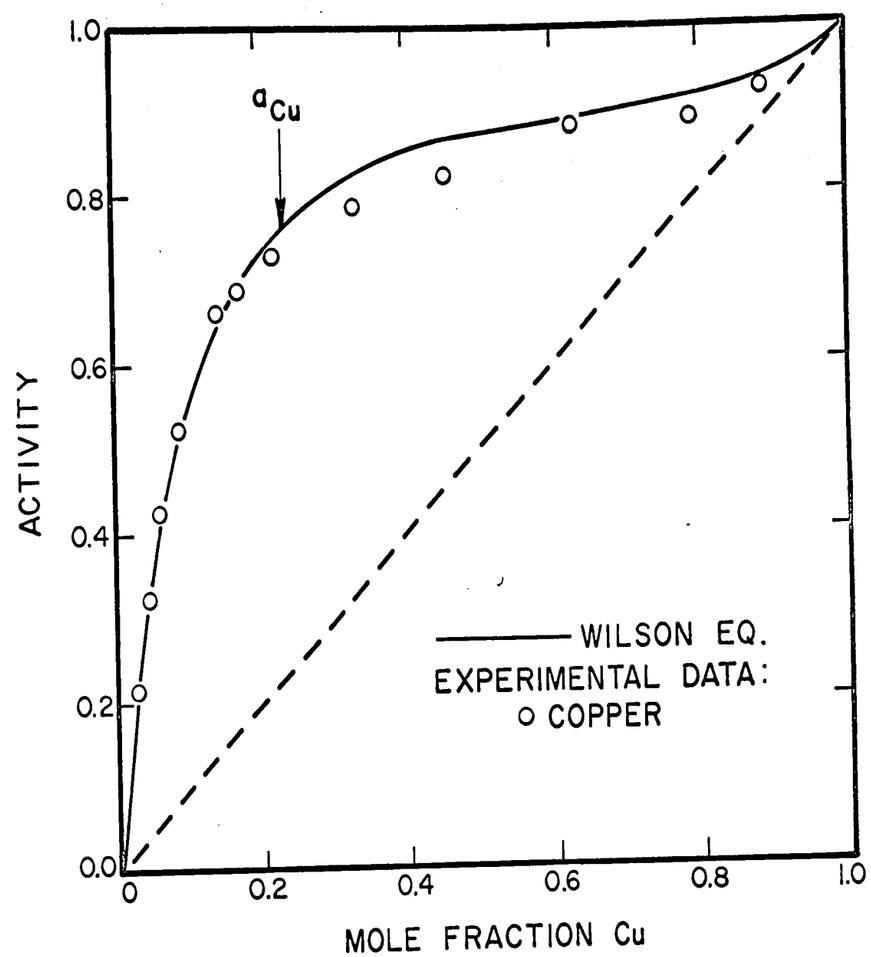

Fig.10. Activities in iron-copper binary alloys at 1550°C. (Expt. data from Morris and Zellars[14].)

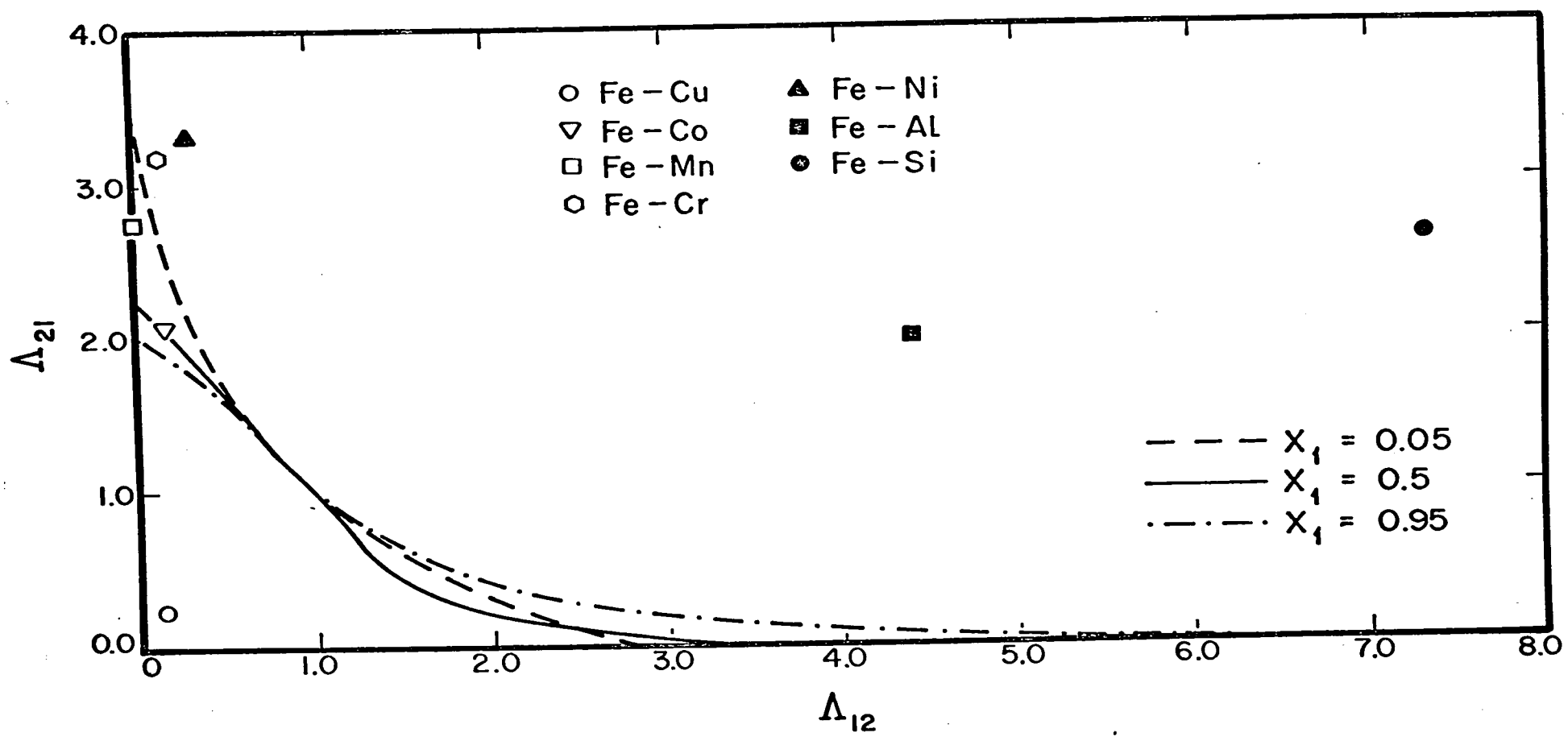

Fig.11. Binary iron-base systems and their relation to ideal behavior of component 1.

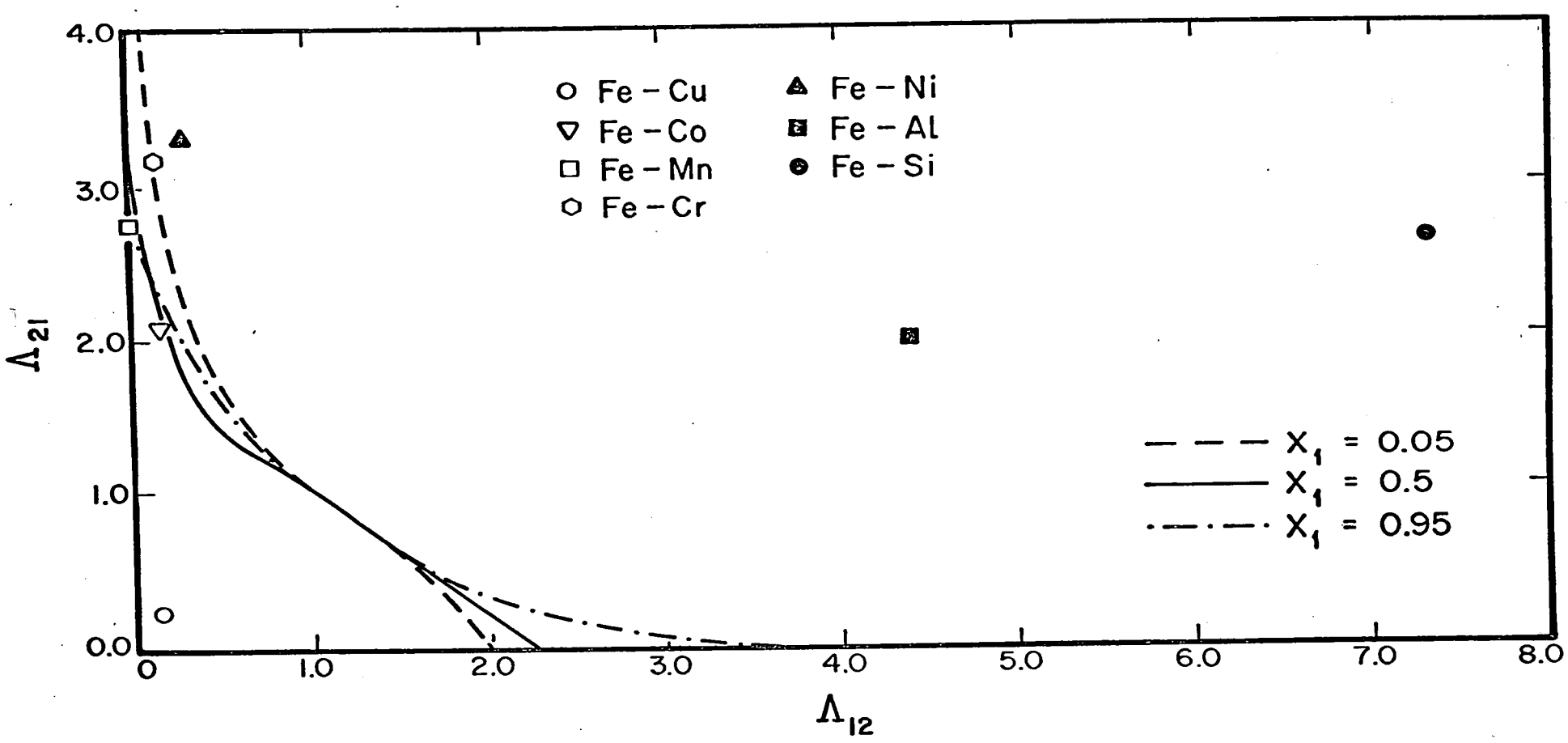

Fig.12. Binary iron-base systems and their relation to ideal behavior of component 2.

APPENDIX

COMPUTER PROGRAM FOR FITTING DATA BY WILSON EQUATION

Page one contains comments about the program and a discussion of control card values. On the second page of the program are the commands to read and print the values that appear on the first data card, the control card. The information entered on this card gives the following: the number of x_1 versus γ_2 and the number of x_1 versus γ_1 experimental points to be considered; the number of Λ_{12} and Λ_{21} Wilson constants to be considered; the initial Λ_{12}, Λ_{21} point where the search will begin; and the values by which the Λ_{12} and Λ_{21} Wilson constants will be incremented. Also printed on this card is information to control the print out of calculated activity coefficients and information to control variations in the program depending on the type of experimental data entered. Also on the second page, the experimental data for the system being considered are read and commands to print these data are given. Next, the first trial value of Λ_{21} as controlled by the data entered on the control card is set. Then a value of Λ_{12} as indicated by the control card is chosen. On pages four, five, and six for the chosen pair of Wilson constants, activity coefficients are calculated for each experimental mole fraction value. Each calculated activity coefficient is subtracted from its corresponding experimental activity coefficient. This deviation is then squared, and all squared deviations for a given selection

of two Wilson constants are summed. As can be seen on page five, the $\Sigma(\gamma_{Calc} - \gamma_{Expt})^2$ value just calculated is stored and a new value of Λ_{12} is chosen. This Λ_{12} value that is chosen is based on the increment that was designated on the control card. After the Λ_{12} value has been changed the procedure described above is repeated and another $\Sigma(\gamma_{Calc} - \gamma_{Expt})^2$ value is calculated and stored. After the designated number of Λ_{12} values have been tried, a new Λ_{21} value is chosen with all the Λ_{12} values successively being paired with the new Λ_{21} value. Then this procedure is repeated until each of the Λ_{21} values has been tried with all of the Λ_{12} values.

Then, as can be seen on pages six and seven all of the $\Sigma(\gamma_{Calc}-\gamma_{Expt})^2$ deviations that have been stored for each Λ_{21} versus Λ_{12} pair of Wilson constants are printed in a data map. An example of this map is shown on page eight of the computer printout. By visual scanning a minimum area or minimum point in the $\Sigma(\gamma_{Calc}-\gamma_{Expt})^2$ values for the Λ_{21} versus Λ_{12} grid can be observed. Then a new range and smaller increments for Λ_{21} and Λ_{12} can be set by changing the data on the control card. For all the calculations that were made for this research work only three or four reductions in the incremental sizes of Λ_{21} and Λ_{12} were necessary to produce Wilson constants to two decimal places.

```
      PROGRAM TSOG(INPUT,OUTPUT)
C
C   THIS PROGRAM ACCOMPLISHES THE FOLLOWING
C
C   A.  PRODUCES A DATA MAP OF LAM12 VS LAM21
C     1. LAM21 AND LAM12 ARE THE 2 PARAMETERS IN THE WILSON EQUATION
C        CHARACTERISTIC OF THE BINARY SYSTEM BEING CONSIDERED
C     2. THESE VALUES OF LAM12 AND LAM21 ARE DETERMINED BY MINIMIZING
C        THE SUM OF THE SQUARE OF THE DIFFERENCES BETWEEN THE CALCULATED
C        AND THE EXPERIMENTAL GAMMA VALUES (ACTIVITY COEFFICIENTS)
C        FOR THE TRIAL VALUES OF LAM21 AND LAM12
C   B.  VALUES OF GAMMA1 AMD GAMMA2 FOR EACH TRIAL PAIR OF LAM12 AND
C        LAM21 CAN BE CALCULATED AND CAN BE PRINTED OUT IF DESIRED
C
C
      DIMENSION X1(500),GAM2(500),SAVE(50,50),WORDS(50),GAM1(50),X11(50)
      REAL LAM21,LAM12,INI21,INI12
C
C   FIRST DATA TO CONTROL THE PROGRAM IS READ
C
C        IDATA TELLS HOW MANY X1 VS GAMMA2 EXPERIMENTAL POINTS ARE BEING
C          CONSIDERED
C        JDATA TELLS HOW MANY X1 VS GAMMA1 EXPERIMENTAL POINTS ARE BEING
C          CONSIDERED
C        L21 IS LIMIT ON LAM21 DO LOOP
C        L12 IS LIMIT ON LAM12 DO LOOP
C        CH21 IS THE INCREMENTAL VALUE FOR THE LAM21 PART OF THE GRID
C        CH12 IS THE INCREMENTAL VALUE FOR THE LAM12 PART OF THE GRID
C        INI21 IS THE POINT IN THE LAM21 SIDE OF THE GRID WHERE THE
C          SEARCH BEGINS
C        INI12 IS THE PCINT IN THE LAM12 SICE OF THE GRID WHERE
C          THE SEARCH BEGINS
C        NO CONTROLS THE PRINT OUT OF CALCULATED GAMMAS
C        IF NO EQUALS 1, THAT IS IF A 1 IS TYPED IN COLUMN 50 ON THE
C         CONTROL CARD THE CALCULATED GAMMA VALUES ARE NOT PRINTED
C        N1 CONTROLS READING AND CALCULATION OF GAMMA2 VALUES
C        IF A 1 IS PRINTED IN COLUMN 54 ON THE CONTROL CARD EXPT GAMMA2
```

```
C          VALUES WILL NOT BE READ AND GAMMA2 CALCULATED VALUES WILL
C          NOT BE DETERMINED
C        N2 CONTROLS READING AND CALCULATION OF GAMMA1 VALLES
C        IF A 1 IS PRINTED IN COLUMN 55 ON THE CONTROL CARD THEN EXPT
C          GAMMA1 VALUES WILL NOT BE READ AND GAMMA1 CALCULATED VALUES
C          WILL NOT BE DETERMINED
C
C
  444 READ 100,IDATA,L21,L12,CH21,CH12,INI21,INI12,NO,JDATA,N1,N2
  100 FORMAT (3I3,4F10.0,I1,I3,2I1)
C
C  PRINT THE CONTROL CARD VALUES
C
      PRINT 300
  300 FORMAT (*1 IDATA L21 L12   CH21   CH12  INI21   INI12   JDATA*/)
      PRINT 302,IDATA,L21,L12,CH21,CH12,INI21,INI12,JDATA
  302 FORMAT (3X,I3,1X,I3,2X,I3,1X,F6.3,2X,F6.3,1X,F6.3,2X,F6.3,4X,I3)
C
C  READ AND PRINT THE EXPERIMENTAL DATA
C
C        X1(I) IS THE MOLE FRACTION OF COMPONENT 1
C        GAM2(I) IS THE ACTIVITY COEFFICINET OF CCMPONENT 2
C        GAM1(I) IS THE ACTIVITY COEFFICIENT OF COMPONENT 1
C
      PRINT 44
   44 FORMAT (//* THIS IS THE EXPERIMENTAL DATA EEING ENTERED*)
      IF(N1.EQ.1) GO TO 850
      PRINT 41
   41 FORMAT (*           X1    GAMMA2*/)
      DO 700 L=1,IDATA
      READ 10,X1(L),GAM2(L)
   10 FORMAT (2F8.4)
  700 PRINT 43,X1(L),GAM2(L)
   43 FORMAT (5X,2F8.4)
  850 CONTINUE
      IF(N2.EQ.1) GO TO 860
      PRINT 82
```

```
 82 FORMAT (///*            X1    GAMMA1*/)
    DO 800 M=1,JDATA
    READ 83,X11(M),GAM1(M)
 83 FORMAT (2F8.4)
800 PRINT 84,X11(M),GAM1(M)
 84 FORMAT (5X,2F8.4)
860 CONTINUE
C
C  THE DO 50 LOOP ENTERS TRIAL VALUES OF LAM21
C  AFTER A FIRST VALUE OF LAM21 HAS BEEN ENTERED THE PROGRAM MOVES ON
C  TO THE DO 60 LOOP
C  HERE SUCCESSIVE VALUES OF LAM12 ARE TRIED BEFCRE RETURNING TO THE
C  DO 50 LOOP FOR ANOTHER TRIAL VALUE OF LAM21
C
      LAM21=0.000+INI21
      DO 50 I=1,L21
      LAM21=LAM21+CH21
      IF(NO.EQ.1) GO TO 77
C
C  PRINT THE VALUE OF LAM21 THAT HAS BEEN ENTERED
C
      PRINT 2
    2 FORMAT (*1LAM21*)
      PRINT 3,LAM21
    3 FORMAT (2X,F6.3)
C
C  THE DO 60 LOOP ENTERS SUCCESSIVE TRIAL VALUES OF LAM12
C
   77 LAM12=0.000+INI12
      DO 60 J=1,L12
      LAM12=LAM12+CH12
      IF(NO.EQ.1) GO TO 88
C
C  PRINT THE TRIAL VALUE OF LAM12 THAT HAS BEEN ENTERED
C
      PRINT 600
```

```
  600 FORMAT (1H0)
      PRINT 4
    4 FORMAT (* LAM12*)
      PRINT 5,LAM12
    5 FORMAT (2X,F6.3)
C
C   THE DO 70 LOOP DOES THE CALCULATIONS NECESSARY FOR DETERMINATION
C   OF LN(GAMMA2) AND GAMMA2 FOR THE 2 TRIAL WILSON CONSTANTS BEING
C   CONSIDERED AT THIS PONT IN THE PROGRAM
C
      IF(N1.EQ.1) GO TO 870
      PRINT 450
  450 FORMAT (1H0)
      PRINT 8
    8 FORMAT (30X,*    VALUE OF GM2LC      AND      GM2C*)
      PRINT 451
  451 FORMAT (1H0)
  870 CONTINUE
   88 SUM=0.0
      IF(N1.EQ.1) GO TO 880
      DO 70 K=1,IDATA
      APAR=LAM21/((LAM21*(X1(K)))+(1.0-X1(K)))
      BPAR=LAM12/(X1(K)+(LAM12*(1.0-X1(K))))
      BOTH=BPAR-APAR
      CPAR=((1.0-X1(K))+LAM21*(X1(K)))
      DPAR=ALOG(CPAR)
      TPAR=-DPAR
      GM2LC=TPAR-((X1(K))*(BOTH))
      GM2C=EXP(GM2LC)
C
C   AFTER A CALCULATED VALUE OF GAMMA2 IS DETERMINED THE FOLLOWING
C   PROCEDURE IS FOLLOWED
C   1. THE CALCULATED GAMMA2 IS SUBTRACTED FROM THE EXPERIMENTAL
C      GAMMA2 THAT WAS USED IN THE WILSON EQUATION WITH THE TRIAL
C      VALUES OF THE WILSON CONSTANTS
C   2. THE DIFFERENCE BETWEEN THE CALCULATED AND EXPERIMENTAL VALUES
```

```
C       OF GAMMA IS THEN SQUARED
C    3. THIS VALUE IS STORED AND IS ADDED TO AS ANCTHER EXPERIMENTAL
C       GAMMA2 AND MOLE FRACTION ARE ENTERED
C    4. THE PROCESS IS THEN REPEATED UNTIL ALL THE EXPERIMENTAL DATA HAVE
C       BEEN ENTERED AND A TOTAL SUM OF THE SQUARES OF THE DIFFERENCES
C       IN THE GAMMA2 VALUES HAS BEEN DETERMINED
C    5. THIS VALUE WILL THEN BE PRINTED IN THE APPROPRIATE PLACE IN THE
C       GRID OF THE SUM OF THE SQUARES OF THE DIFFERENCES FOR ALL DATA
C       AND TRIAL VALUES
C
      DIFF=GAM2(K)-GM2C
      SDIF=DIFF*DIFF
      SUM=SUM+SDIF
      IF(NO.EQ.1) GO TO 70
C
C  PRINT THE VALUES OF LN GAMMA2 AND GAMMA2 THAT HAVE BEEN
C  CALCULATED FOR THE RESPECTIVE TRIAL VALUES OF LAM21 AND LAM12
C
      PRINT 9,GM2LC,GM2C
    9 FORMAT (24X,2F20.6)
   70 CONTINUE
  880 CONTINUE
      IF(N2.EQ.1) GO TO 890
      IF(NO.EQ.1) GO TO 930
      PRINT 910
  910 FORMAT (1H0)
      PRINT 920
  920 FORMAT (30X,*   VALUE OF GM1LC      AND      GM1C*/)
  930 CONTINUE
C
C  AFTER A CALCULATED VALUE OF GAMMA1 IS DETERMINED A PROCEDURE SIMILAR
C  TO THAT ABOVE IS FOLLOWED EXCEPT THAT THE SQUARE OF THE DIFFERENCE
C  BETWEEN THE CALCULATED AND EXPERIMENTAL VALUES IS ADDED TO THE
C  SUM DETERMINED ABOVE
C
      DO 80 N=1,JDATA
```

```
      XPAR=LAM21/((LAM21*(X11(N)))+(1.0-X11(N)))
      YPAR=LAM12/(X11(N)+LAM12*(1.0-X11(N)))
      YBOT=YPAR-XPAR
      FPAR=(X11(N)+LAM12*(1.0-X11(N)))
      FPAL=ALOG(FPAR)
      TBOT=-FPAL
      GM1LC=TBOT+((1.0-X11(N))*YBOT)
      GM1C=EXP(GM1LC)
      DIF2=GAM1(N)-GM1C
      SDF2=DIF2*DIF2
      SUM=SUM+SDF2
      IF(NO.EQ.1) GO TO 80
C
C   PRINT THE VALUES OF LN GAMMA1 AND GAMMA1 THAT HAVE BEEN CALCULATED
C   FOR THE RESPECTIVE TRIAL VALUES OF LAM21 AND LAM12
C
      PRINT 900,GM1LC,GM1C
  900 FORMAT (24X,2F20.6)
   80 CONTINUE
  890 CONTINUE
      SAVE(J,I)=SUM
   60 CONTINUE
   50 CONTINUE
C
C   PRINT HEADINGS FOR THE SUM OF THE SQUARE OF THE DIFFERENCES GRID
C
      PRINT 410
  410 FORMAT (1H1)
      PRINT 404
  404 FORMAT (*          FOR THE STATED PAIR OF TRIAL VALUES OF LAM21*/)
      PRINT 405
  405 FORMAT (*          AND LAM12, EACH NUMBER IN THE FOLLOWING GRID*/)
      PRINT 406
  406 FORMAT (*          IS THE SUM OF THE SQUARES OF DIFFERENCES*/)
      PRINT 407
  407 FORMAT (*          BETWEEN CALCULATED AND EXPERIMENTAL GAMMA2*/)
```

```
      PRINT 408
  408 FORMAT (*                VALUES FOR EACH GAMMA2 VALUE IN A DATA SET*/)
      PRINT 520
  520 FORMAT (*                PLUS THE SUM OF THE SQUARES OF THE*/)
      PRINT 530
  530 FORMAT (*                DIFFERENCES BETWEEN CALCULATED AND EXPT*/)
      PRINT 540
  540 FORMAT (*                GAMMA1 VALUES FOR EACH GAMMA1 VALUE IN A*/)
      PRINT 550
  550 FORMAT (*                DATA SET*/)
      PRINT 420
  420 FORMAT (1H0)
C
C  THE FOLLOWING A FORMAT ENTERS INFORMATICN ABOLT
C  PARTICULAR GRID BEING CONSIDERED
C
      READ 400,(WORDS(I),I=1,16)
  400 FORMAT (8A10)
      PRINT 401,(WORDS(I),I=1,16)
  401 FORMAT (10X,8A10/,10X,8A10)
C
C  THE FOLLOWING SECTION PRINTS THE GRID OF LAM12 VS LAM21
C
      PRINT 480
  480 FORMAT (1H0)
      READ 350,FORM
  350 FORMAT (A10)
      DO 7 J=1,L12
      PRINT FORM,(SAVE(J,I),I=1,L21)
    7 CONTINUE
      END
```

FOR THE STATED PAIR OF TRIAL VALUES OF LAM21
AND LAM12, EACH NUMBER IN THE FOLLOWING GRID
IS THE SUM OF THE SQUARES OF DIFFERENCES
BETWEEN CALCULATED AND EXPERIMENTAL GAMMA2
VALUES FOR EACH GAMMA2 VALUE IN A DATA SET
PLUS THE SUM OF THE SQUARES OF THE
DIFFERENCES BETWEEN CALCULATED AND EXPT
GAMMA1 VALUES FOR EACH GAMMA1 VALUE IN A
DATA SET

FOR FE-AL//LAM21 AXIS, LEFT-RIGHT, FROM 0.50 TO 3.000, INCREMENT OF 0.50
FOR FE-AL//LAM12 AXIS, TOP-BOTTOM, FROM 0.50 TO 5.000, INCREMENT OF 0.50

28.76948	12.94535	6.94795	4.16490	2.71328	1.89478
13.02307	5.80065	3.06665	1.80949	1.16831	.82222
6.98095	3.03880	1.54681	.87563	.54951	.38921
4.13058	1.73073	.82793	.43647	.26148	.19058
2.61133	1.03561	.45144	.21198	.11927	.09703
1.73040	.63817	.24308	.09409	.05033	.05697
1.18789	.40053	.12575	.03440	.02177	.04668
.83929	.25543	.06146	.00879	.01696	.05402
.60889	.16714	.02980	.00417	.02681	.07224
.45422	.11537	.01908	.01297	.04597	.09734